Structure and Property Development of Poly(3-hexylthiophene) Organogels Probed with Combined Rheology, Conductivity and Small Angle Neutron Scattering

Gregory M. Newbloom[‡], *Katie M. Weigandt*[‡] *and Danilo C. Pozzo**

Department of Chemical Engineering, University of Washington, Box 351750, Seattle,
Washington 98195-1750, United States

* E-mail: dpozzo@u.washington.edu. ‡These authors contributed equally.

SUPPORTING INFORMATION

Scattering Length Density. The scattering length density can be easily calculated when both the molecular formula and density of a material are precisely known:

$$\rho_{Solvent}^{SLD} = \frac{\sum_{i=1}^{n} b_{c_i}}{v_m} \tag{S1}$$

where $\rho_{Solvent}^{SLD}$ is the scattering length density, b_{c_i} is the bound coherent scattering length of each atom in the molecule and v_m is the molecular volume. The mass density ($\rho_{Solvent}^{m}$) is directly related to molecular volume and therefore the temperature dependence of mass density will play a role in the scattering length density. The mass density of d10-pxylene, d8-toluene and d6-benzene was measured as a function of temperature using an Anton Paar DMA 5000 Density Meter and then converted to scattering length density, seen in Figure S2. This temperature dependence was accounted for during SANS data fitting to ensure the accuracy of other fitting parameters.

Specific Surface Area Analysis. The Porod analysis can be applied to the scattering of any two-phase system with a sharp interface that leads to an $I(q) \propto q^{-4}$ dependence at high-q. The evolving P3HT gel is effectively a three-component system containing solvent, P3HT fibers and dissolved P3HT chains. In order to find the specific surface area (S_v) of the P3HT fiber, the scattering due to the dissolved polymer must first be subtracted. The scattering of the fully dissolved polymer, at elevated temperatures (40 ºC to 80 ºC), was fit with a model for polymers with excluded volume interactions to determine the molecular weight and conformation in solution.

The mass balance presented in Equation 1 of the paper can then be utilized to determine the fraction of polymer in fiber form (Ψ_f):

$$I(q)=\phi_v\Psi_f(\Delta\rho_{PP})^2 P_{PP}(q)+\phi_v(1-\Psi_f)(\Delta\rho_{PExV})^2 P_{PExV}(q) \tag{1}$$

which means that the pre-factor $(1-\Psi_f)$ can also be utilized to determine the fraction of P3HT in dissolved form. The model for polymers with excluded volume interactions can be scaled by this factor and subtracted from the combined SANS profile to yield the scattering corresponding only to P3HT fibers.

Figure S3a shows the SANS profile for 30 mg/mL P3HT in toluene at a specific temperature (10.6 ºC) during the gelation of P3HT. The fraction of P3HT in fiber from (Ψ_f) was determined to be 0.419 by fitting Equation 1 to the SANS profile. This leads to a dissolved fraction $(1-\Psi_f)$ of 0.581 at the same temperature. The total scattering as a function of q due to the dissolved polymer alone can be determined by scaling the model for polymers with excluded volume interactions (Equation 3) by the dissolved fraction. The result can be seen in Figure S3a.

$$P_{PExV}(q,n,a,v)=2\int_0^1 d\ \ (1-xx)\exp\left[-\frac{q^2a^2}{6}n^{2v}x^{2v}\right] \tag{3}$$

The 1D SANS profile is a linear combination of the dissolved polymer phase and the fiber phase, so we can directly subtract the scaled dissolved polymer model from the "fiber + dissolved" polymer scattering to generate the scattering due to P3HT fibers alone. This subtraction is shown to generate the expected $I(q)\propto q^{-4}$ dependence for P3HT fibers, as seen in Figure S3a. We find this same result to be true at earlier stages in gelation, to Ψ_f as low as 0.03. This behavior is shown as a function of gelation progress (i.e. temperature) in Figure S3b which highlights the $I(q)\propto q^{-4}$ dependence.

After the dissolved polymer is subtracted, the scattering invariant (Q) can be utilized to directly calculate the fiber volume fraction (ϕ_{fiber}).[1, 2]

$$Q=\int_0^\infty I(q)\cdot q^2\,dq=2\pi^2\phi_{fiber}\left(1-\phi_{fiber}\right)\left(\Delta\rho_{PP}\right)^2 \tag{S2}$$

The invariant can be utilized with minimal assumptions and regardless of the shape of the scattering object. At low-q, the slope associated with the network structure of P3HT gels (seen in Figure S3a) has to be extrapolated to q = 0 but the extrapolation only accounts for < 0.5% of the total scattering invariant (Q). At high-q, the $I \propto q^{-4}$ dependence associated with the Porod slope (seen in Figure S2) is also extrapolated to$\rightarrow$q∞ and this accounts for ~ 7% of the total invariant. This means that ~ 93% of the scattering invariant (Q) is directly accounted for in the

SANS profile, leading to low error in the calculation of the volume fraction of fibers (ϕ_{fiber}). There is also, on average, a less than 10% difference between ϕ_{fiber} calculated from the scattering invariant (Q) and ϕ_{fiber} calculated from the form factor fitting ($\phi_{fiber} = \phi_v \cdot \Psi_f$). The small differences between these independent determinations of ϕ_{fiber} support the accuracy of the S_v calculations.

SANS Molecular Weight Determination. The weight-averaged molecular weight (M_w) can be directly calculated from SANS of dissolved polymer chains (Equation S3):[3]

$$M_w = \frac{N_A \cdot \left(\rho^{m}_{P3HT}\right)^2 \cdot I(0)}{c \cdot (\Delta\rho_{PExV})^2} \tag{S3}$$

where N_A is Avogadro's number, c is the concentration of dissolved P3HT in solution, ρ^{m}_{P3HT} is the mass density of P3HT chains (1.1 g/cm^3), $I(0)$ is the absolute-scaled scattering intensity at $q = 0$ and $\Delta\rho_{PExV}$ is the scattering contrast between solvent and dissolved polymer chains.

Impedance Spectroscopy Fitting. A frequency sweep, from 20 – 2,000,000 Hz, of the fully developed gel phase was performed between the stainless steel parallel plate electrodes of the dielectric-rheology experimental setup. The linearized impedance spectroscopy is presented in Figure 7b of the main text. These data sets are fit with a simple equivalent circuit: a resistor (R_s) in series with a parallel resistor (R_p) and constant phase element capacitor (CPE). This equivalent circuit leads to the following equation:

$$Z = R_s + \frac{R_p}{\tau \cdot (j \cdot \omega)^{\alpha}} \tag{S4}$$

where τ is a constant in units $F\,cm^{-2} s^{\alpha-1}$ and α is the constant phase element.[4, 5] The resistance (R_p) can be converted to dc conductivity (σ) using Equation S5, where d is the distance between electrodes and A is the surface area of the electrode. The fitting results are summarized in Table S1.

$$\sigma = \frac{1}{R_p} \cdot \frac{d}{A} \tag{S5}$$

REFERENCES

1. G. M. Newbloom, K. M. Weigandt and D. C. Pozzo, *Macromolecules*, 2012, **45**, 3452-3462.

2. J. J. Richards, K. M. Weigandt and D. C. Pozzo, *J. Colloid Interface Sci,*. 2011, **364**, 341-350.

3. J. Plestil, H. Pospisil, Y. M. Ostanevich and G. Degovics, *J. of Appl. Crystallogr.*, 1991, **24**, 659-664.

4. J.-B. Jorcin, M. E. Orazem, N. Pébère and B. Tribollet, *Electrochim. Acta*, 2006, **51**, 1473-1479.

5. A. Lasia, Impedance of Porous Electrodes. In *Modern Aspects of Electrochemistry*, R. E. White, B. E. Conway and J. O. Bockris (Eds.); Kluwer Academic/Plenum Publishers: New York, 1999, pp 143.

SUPPORTING FIGURES

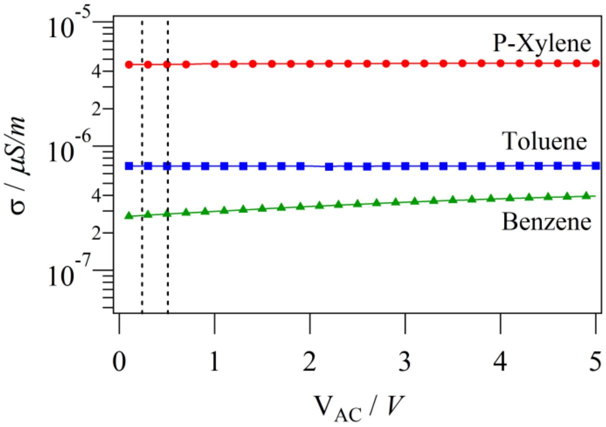


Figure S1. AC voltage sweep at 2 kHz of 30 mg/mL P3HT organogels formed in different organic solvents. Dashed lines represent the V_{AC} utilized for dielectric-SANS (0.2 V) and dielectric-rheology (0.6 V) experiments.

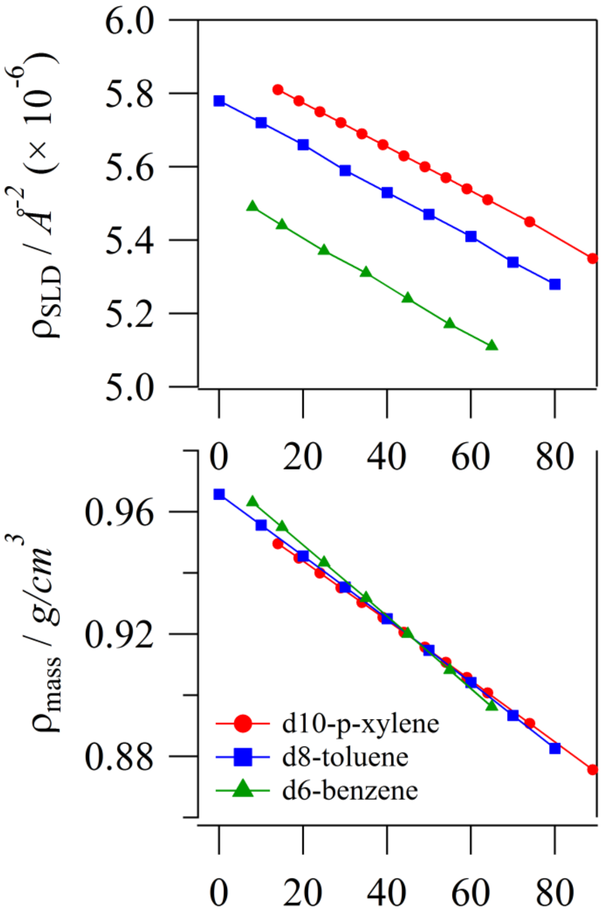


Figure S2. The temperature dependence on the measured mass density and subsequently calculated scattering length density of d10-p-xylene (d > 98%), d8-toluene (d > 99.5%) and d6-benzene (d > 99.5%).

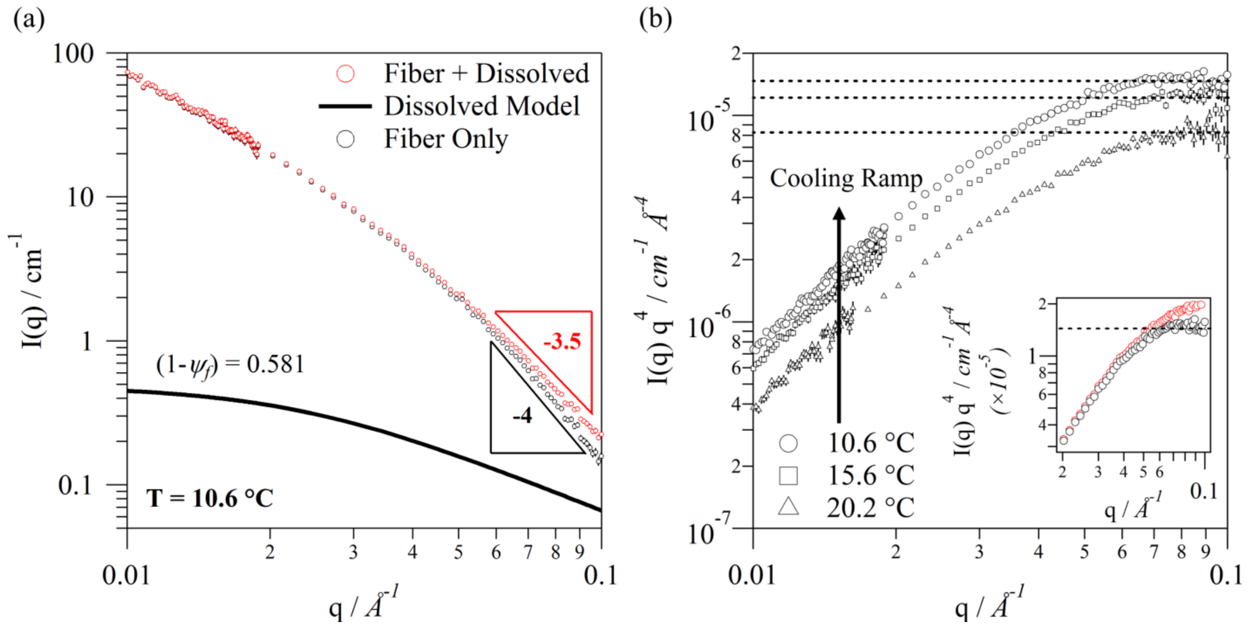


Figure S3. (a) SANS profiles from the cooling ramp and gelation of 30 mg/mL P3HT in d8-toluene at 10.6 ºC. “Fiber + dissolved” (i.e. unmodified scattering) is represented by ○, the polymer excluded volume model scaled by $(1-\Psi_f)$ is represented by —, and the “fiber only” is represented by ○. At high-q, the difference between the “fiber + dissolved” scattering slope and the “fiber only” slope is compared. (b) The $I(q) \sim q^{-4}$ is evaluated for multiple “fiber only” SANS profiles at differing temperatures from the same cooling ramp. The horizontal dashed lines represent the values extracted for the Porod analysis. The inset figure highlights the differences at high-q for 10.6 ºC scattering for “fiber + dissolved” and “fiber only” scattering.

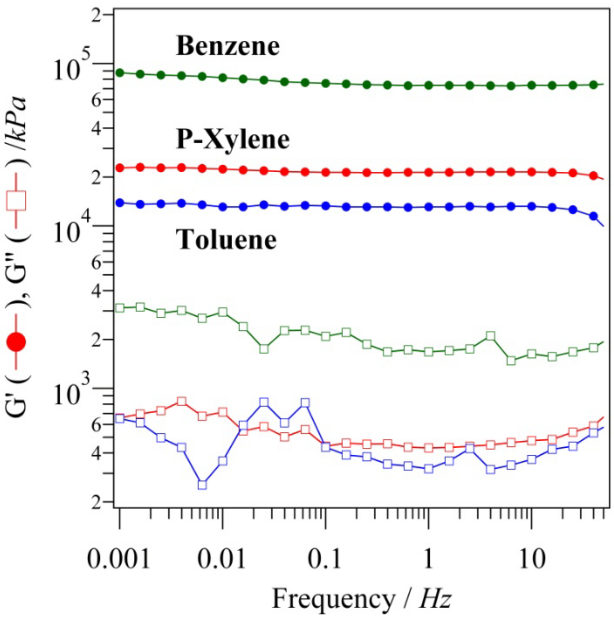
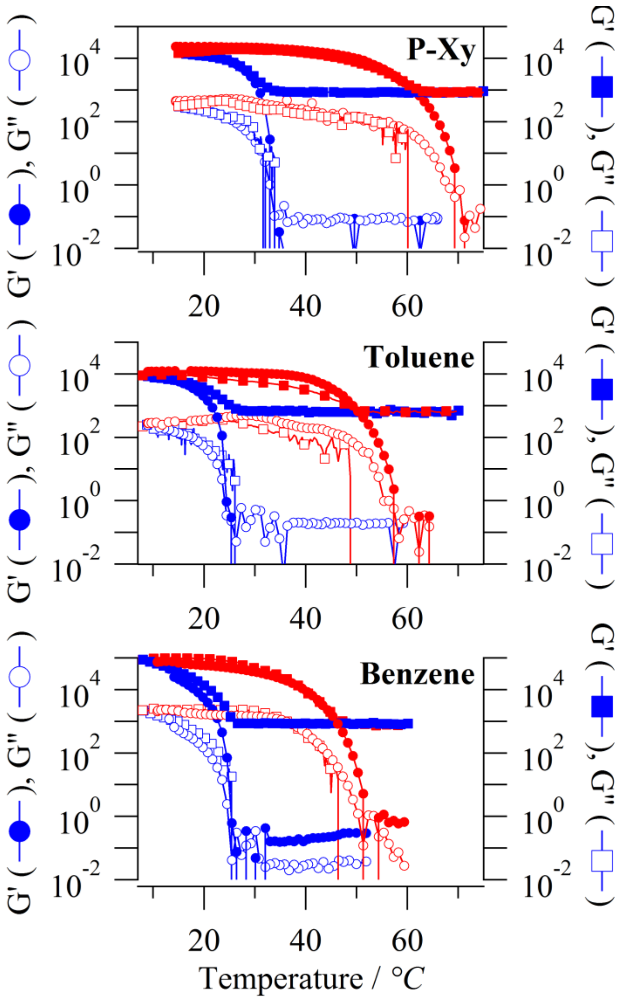


Figure S4. Rheological frequency sweep of fully-developed P3HT organogels in different aromatic solvents.



.

Figure S5. Rheology-SANS (left axis) and dielectric-rheology (right axis) of P3HT organogels formed and dissolved in p-xylene, toluene and benzene where *G'* is the elastic modulus and *G"* is the loss modulus. Blue markers represent the cooling ramp (gelation) while red markers represent the re-heating ramp (re-dissolution).

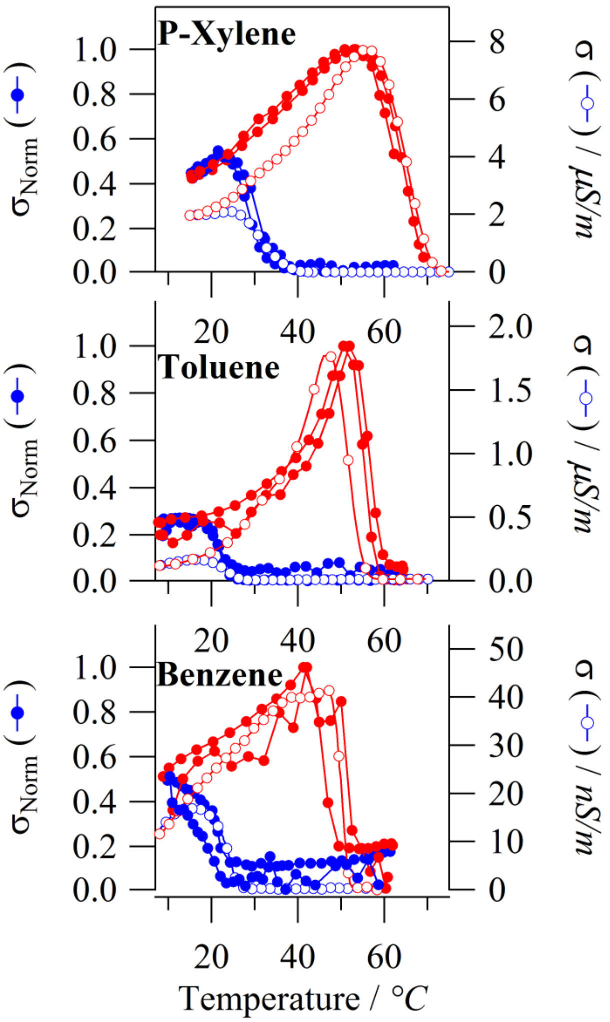


Figure S6. Normalized conductivity from dielectric-SANS (left axis) and ac conductivity of dielectric-rheology (right axis) for P3HT organogels formed (blue) and re-dissolved (red) in different organic solvents.

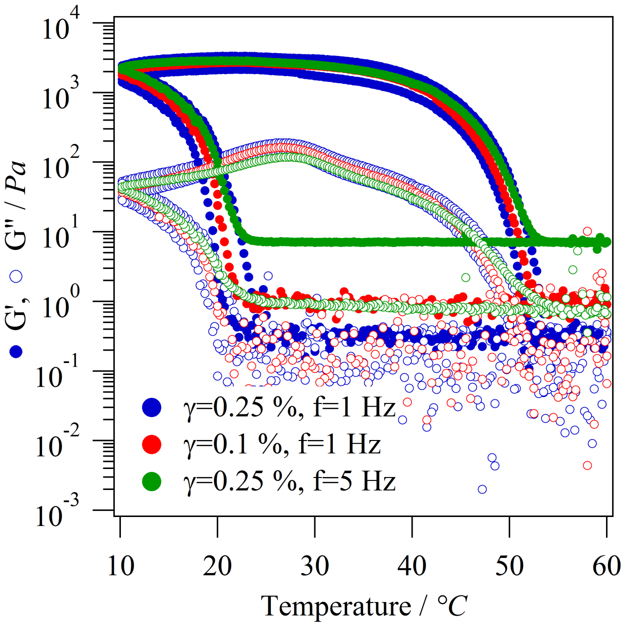


Figure S7. Temperature dependent rheology of a 30 mg/mL gel in toluene run under three separate measurement conditions. The $\gamma = 0.25\%$, $f = 1$ Hz oscillation data corresponds to the measurements reported in the main text. The transition temperatures and curve shapes are largely independent of the measurement conditions. When using the higher frequency (5 Hz) the apparent modulus in the dissolved state is also higher due to instrument inertia.

Table S1. Equivalent circuit fitting results of electrochemical impedance spectroscopy from fully developed 30 mg/mL P3HT organogels formed in different organic solvents. This linearized impedance data is fit with Equation S4.

	P-Xylene	**Toluene**	**Benzene**
R_s **(Ω)**	1110	762	47
R_p **(MΩ)**	0.160	1.155	58.89
$\tau\,(F\,cm^{-2}s^{\alpha-1})$	1.00×10^{-10}	3.42×10^{-11}	2.30×10^{-11}
α	0.862	0.944	0.991